

PCTWORLD INTELLECTUAL PRO
International

INTERNATIONAL APPLICATION PUBLISHED UNDER

(51) International Patent Classification⁶ :

C22C 18/04, H01M 4/42

A1

(11)

WO 9607765A1

(43) International Publication Date:

14 March 1996 (14.03.96)

(21) International Application Number: PCT/EP95/03350

(22) International Filing Date: 23 August 1995 (23.08.95)

(30) Priority Data:
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Gulledelle 92, B-1200 Brussels (BE).(81) Designated States: AM, AU, BB, BG, BR, BY, CA, CN, CZ,
EE, FI, GE, HU, IS, JP, KG, KP, KR, KZ, LK, LR, LT,
LV, MD, MG, MK, MN, MX, NO, NZ, PL, RO, RU, SG,
SI, SK, TJ, TM, TT, UA, US, UZ, VN, European patent
(AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC,
NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA,
GN, ML, MR, NE, SN, TD, TG), ARIPO patent (KE, MW,
SD, SZ, UG).

Published

With international search report.

(54) Title: ZINC POWDER FOR ALKALINE BATTERIES

(57) Abstract

A zinc powder for alkaline batteries consists of 0.0005-1 % of aluminium, 0.001-2 % of at least one of bismuth, indium and gallium, one or several elements of the group of elements consisting of magnesium, strontium, barium and REM such that the ratio between the number of moles of aluminium and the number of moles of that element or the sum of the number of moles of the several elements amounts at most to 2 and such that the sum of the concentrations of aluminium and that element or those elements amounts at most to 2 %, and possibly Ca such that the ratio between the number of moles of aluminium and the sum of the number of moles of calcium and of that element or the sum of the number of moles of calcium and of those elements amounts at most to 2 and such that the sum of the concentrations of aluminium, calcium and that element or those elements amounts at most to 2 %, the remainder being zinc; REM being a rare earth metal or a mixture of rare earth metals. This powder can comprise up to 20 ppm of iron.

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ZINC POWDER FOR ALKALINE BATTERIES

This invention relates to an aluminium-containing zinc powder for alkaline batteries.

Aluminium-containing zinc powders are known from EP-A-0427315. In this document protection is sought for a powder based on zinc for alkaline batteries, characterized in that it comprises 0.005-2% of aluminium as well as either 0.0001-0.01% of REM, REM being a rare earth metal or a mixture of rare earth metals; or, apart from zinc and unavoidable impurities, exclusively 0.0001-2% of at least one of indium and REM ; or, apart from zinc and unavoidable impurities, exclusively 0.003-2% of bismuth and 0.0001-2% of at least one of indium and REM ; or, apart from zinc and unavoidable impurities, exclusively 0.005-2% of lead and 0.0001-2% of at least one of indium and REM ; or, apart from zinc and unavoidable impurities, exclusively 0.005-2% of lead, 0.003-2% of bismuth and 0.0001-2% of at least one of indium and REM.

The first example from this document relates to a powder which is made by atomizing a solution with the following composition : 220 ppm Al, 5 ppm La, 12 ppm Ce, 500 ppm Pb, 54 ppm In, the remainder being thermally refined zinc. The second example relates to a powder which is made by atomizing a solution with composition : 600 ppm Al, 500 ppm Pb, 500 ppm Bi, 100 ppm In, the remainder being thermally refined zinc. All other examples described concern powders with aluminium contents ranging from 0.03 to 0.06% and with possible REM contents ranging from 0.004 to 0.006% (all percentages stated above or in the following are percentages by weight).

The powders according to these examples all have good resistance to corrosion in the electrolyte of the battery before and after partial discharge of the battery. They exhibit, however, the disadvantage that in certain types of batteries, for example the LR6 type, they can give rise to short circuits in the battery.

The object of the invention is to provide an aluminium-containing zinc powder for alkaline batteries that gives rise in much lower measure than the powders according to the examples from EP-A-0427315, or not at all, to short circuiting and that at the same time has a satisfactory corrosion resistance.

The powder of the invention is characterized in that it consists of

- (a) 0.0005-1% of aluminium,
- (b) at least one of magnesium, strontium, barium and REM in such concentration that the ratio between Al, expressed in moles, and the sum of Mg, Sr, Ba and REM, expressed in

moles, amounts at most to 2 and that the sum of the concentrations of Al, Mg, Sr, Ba and REM amounts at most to 2%,

(c) 0.001-2% of at least one of bismuth, indium and gallium,

(d) possibly calcium in such concentration that the ratio between Al, expressed in moles,

5 and the sum of Ca, Mg, Sr, Ba and REM, expressed in moles, amounts at most to 2, and that the sum of the concentrations of Al, Ca, Mg, Sr, Ba and REM amounts at most to 2%.

(e) the remainder being zinc.

10 By zinc is meant here and in the following thermally or electrolytically refined zinc (Special High Grade).

The applicant forgoes, however, protection for the following composition according to the invention : Zn - 0.003 % Al - 0.01 % Sr - 0.003 % Bi - 0.05 % In, as that composition is mentioned in JP-A-06005284.

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In fact, the applicant has found that zinc powder which at the same time comprises aluminium, at least one of Mg, Sr, Ba and REM, and possibly Ca in the concentrations defined above gives rise to nearly no or no short circuits in the battery in which it is used. At the same time the applicant has found that these powders can comprise up to 20 ppm Fe and then still have a suitable corrosion resistance, in particular after partial or complete discharge of the battery. The other alloying elements (Bi and/or In and/or Ga) give the powder an adequate corrosion resistance before discharge. The powder is thus also suitable for use in any type of battery, such as LR6, LR14, LR20 and others.

20 The iron that the powder can comprise consists of the iron present as unavoidable impurity in the zinc and in the alloying elements and of the iron that is accidentally introduced into the powder during its preparation.

25 Here, it should be noted that JP-A-06005284 relates to zinc powders for alkaline batteries containing 0.01-0.1 % In, 0.001-0.01 % Bi, 0.001-0.01 % Al and 0.001-0.01 % of at least one selected from the group consisting of Ti, Mn, Co, Ni and Sr. When one uses these powders in battery types having a sealed structure such as cylindrical alkaline or manganese battery, it is necessary to add to the electrode, as anti-corrosive, 0.005-0.5 % indium chemicals and/or 0.0001-0.05 % tetrabutylammonium hydroxide in order to obtain a leakproof battery which can be put in practical use.

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REM can be any rare earth metal, such as for example La, Ce, Pr, Sm, Gd or Nd, or any mixture of rare earth metals, such as for example a mixture of La and Ce. For economic reasons, REM is preferably a mixed metal, an alloy with mainly La and Ce and a little, for example $\leq 10\%$ of other rare earth metals.

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The ratio between the number of moles of Al and the number of moles of Mg, Sr, Ba and/or REM and possibly Ca amounts at most to 2, as at higher values short circuits can occur. The ratio is preferably at most 1.5, and especially at most 1.

5 The sum of the concentrations of Al and Mg, Sr, Ba and/or REM and possibly Ca amounts at most to 2%, preferably at most to 1%, and especially at most to 0.2%. It is clear that when the powder has a fairly high Fe content, then the minimum quantity of Al and Mg, Sr, Ba and/or REM and possibly Ca which must be added in order to obtain a suitable corrosion resistance will be higher than in the case of the powder having a low Fe content.

10 Further preferred compositions of the powder according to the invention form the object of the appended Claims 6-22.

A simple manner of producing the powder of the invention consists in adding all
15 additives which should be present in the powder to be produced (for example Al, Ba and Bi) to molten zinc and to atomize the alloy so obtained with gas, water or a mixture of both. It is also possible to atomize molten zinc that already comprises a portion of the additives (for example Al and Ba), after which the remainder of the additives (for example In) are deposited on the atomized powder, either by cementation from an aqueous solution, or by
20 physical deposition from a gas phase ("Physical Vapour Deposition" or PVD), or by chemical deposition from a gas phase ("Chemical Vapour Deposition" or CVD). It is clear that the cementation technique can only be applied when dealing with additives which are more electropositive than zinc. When several additives are to be deposited on the atomized powder, these can be deposited simultaneously or separately.

25 It is also possible to introduce a particular additive partially via the molten zinc and the rest of it by deposition on to the atomized powder.

Instead of atomizing with gas, water or a mixture of both, any technique can be applied which is suitable for converting a molten metal to a powder, such as for example centrifugal atomization or casting and breaking up the cast metal.

30 If the desired powder contains additives capable of cementation (for example In or Ga), then yet another manner of preparing the powder of the invention consists in preparing a powder with the additives which are not capable of cementation, and possibly a portion of the additives which are capable of cementation, according to one of the methods described above and from the powder so obtained to make an anode which is fitted in the battery. The
35 additives which are capable of cementation are added to the electrolyte of the battery, from where they cement on to the powder of the anode. Thus the powder according to the invention is obtained in the battery itself.

This invention thus not only relates to a powder which can be introduced into the battery, but also to a powder which is present in the battery.

The examples described in the following, demonstrate that powders according to the invention do not cause short circuiting in the battery and have good resistance to corrosion in the electrolyte of the battery after partial discharge of the battery.

5 10 powders were made with the following composition :

- (1) Zn - 70 ppm Al - 500 ppm Bi - 500 ppm In
- (2) Zn - 30 ppm Al - 500 ppm Bi - 500 ppm In
- (3) Zn - 70 ppm Al - 500 ppm Bi - 500 ppm In - 7 ppm La - 12 ppm Ce
- 10 (4) Zn - 70 ppm Al - 500 ppm Bi - 500 ppm In - 153 ppm La - 360 ppm Ce
- (5) Zn - 70 ppm Al - 500 ppm Bi - 500 ppm In - 115 ppm Sr
- (6) Zn - 70 ppm Al - 500 ppm Bi - 500 ppm In - 550 ppm Sr
- (7) Zn - 70 ppm Al - 500 ppm Bi - 180 ppm Sr
- (8) Zn - 30 ppm Al - 250 ppm Bi - 250 ppm In - 200 ppm Sr
- 15 (9) Zn - 70 ppm Al - 500 ppm Bi - 90 ppm Sr - 130 ppm Ca
- (10) Zn - 70 ppm Al - 500 ppm Bi - 500 ppm In - 440 ppm Ba

For this purpose, the starting point is refined zinc in fluid state to which the alloying elements are added in the desired quantities. The molten zinc solution thus obtained is
20 homogenized at 450°C by stirring. The molten alloy is allowed to flow away in a stream of gas and in this way an alloy powder is produced, the particles of which have nearly the same homogeneous composition as that of the homogeneous molten solution.

The alloy powder is sieved so that the fraction which is larger than 500 µm and, in so
25 far as this is possible, the fraction that is smaller than 104 µm is separated from it. In this way an alloy powder is obtained with a particle size distribution of 104 to 500 µm. The powders (1)-(3) are powders according to the previously mentioned prior art and the powders (4)-(10) are powders according to the invention.

30 With the alloy powder are then made

- batteries of the type LR14
 - batteries of the type LR6 in which a commercial separator is used which has low density.
- The LR14 batteries are discharged at 2.2 ohms for 6 h and then the quantity of hydrogen liberated is determined. The LR6 batteries are discharged discontinuously in order to check
35 whether a premature fall of the discharge curve occurs as a result of short circuiting. The results of both tests are presented summarized in the table below.

Powder No.	Fe ppm	mol Al/ Σ mol Mg, Sr, Ba, REM and/or Ca	Gas μ l/g/day	Short circuiting
(1)	≤ 1	—	64	yes
(2)	≤ 1	—	104	yes
(3)	≤ 1	19.1	75	yes
(4)	≤ 1	0.71	65	no
(5)	≤ 1	1.98	39	no
(6)	1	0.41	50	no
(7)	≤ 1	1.26	75	no
(8)	2	0.49	98	no
(9)	2	0.61	73	no
(10)	3	0.81	78	no

Comparison of examples nos. (1)-(3) with examples nos. (4)-(10) shows that the powders according to the invention have a good corrosion and do not give rise to short circuiting in the battery.

Other typical examples of powders according to the invention have the following composition:

Zn - 50 ppm Al - 100 ppm La - 100 ppm Ce - 500 ppm In

Zn - 100 ppm Al - 420 ppm Ba - 500 ppm In

Zn - 100 ppm Al - 300 ppm Ba - 500 ppm Bi

Zn - 250 ppm Al - 500 ppm Mg - 500 ppm Bi

Zn - 500 ppm Al - 1000 ppm Mg - 500 ppm Bi

Zn - 250 ppm Al - 500 ppm Sr - 500 ppm Ga

Zn - 480 ppm Al - 1000 ppm Sr - 500 ppm Ga

Zn - 100 ppm Al - 150 ppm La - 150 ppm Ce - 250 ppm In - 250 ppm Bi

Zn - 500 ppm Al - 150 ppm Mg - 700 ppm Ba - 500 ppm In - 500 ppm Bi

Zn - 80 ppm Al - 200 ppm Sr - 250 ppm In - 250 ppm Bi

Zn - 100 ppm Al - 80 ppm Mg - 100 ppm Ca - 250 ppm Ga - 250 ppm Bi

Zn - 120 ppm Al - 100 ppm Sr - 150 ppm Ca - 500 ppm Ga - 250 ppm Bi

Zn - 500 ppm Al - 100 ppm La - 100 ppm Ce - 700 ppm Ca - 500 ppm Ga - 500 ppm Bi

Zn - 100 ppm Al - 100 ppm Mg - 100 ppm Sr - 100 ppm Ca - 250 ppm Ga - 250 ppm Bi - 250

ppm In

Zn - 700 ppm Al - 600 ppm Mg - 200 ppm Sr - 1000 ppm Ba - 500 ppm Ga - 500 ppm Bi -
250 ppm In

Zn - 1000 ppm Al - 500 ppm Mg - 100 ppm Sr - 150 ppm La - 150 ppm Ce - 400 ppm Ga -
400 ppm Bi

5 Zn - 400 ppm Al - 1200 ppm Ba - 250 ppm Ga - 400 ppm Bi

Zn - 250 ppm Al - 1200 ppm Ba - 400 ppm Ga

Zn - 750 ppm Al - 1600 ppm Ba - 200 ppm La - 200 ppm Ce - 450 ppm Ga

Zn - 500 ppm Al - 500 ppm Ba - 200 ppm Sr - 250 ppm Ca - 300 ppm Ga

Zn - 350 ppm Al - 100 ppm Sr - 150 ppm La - 150 ppm Ce - 200 ppm Ca - 250 ppm Bi

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These powders comprise, besides zinc, ≤ 20 ppm Fe and the other unavoidable impurities, nothing other than the additives mentioned. The other unavoidable impurities are the impurities which are present in the zinc and in the additives and those accidentally introduced at the time of preparing the powder.

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Claims

1. Aluminium-containing zinc powder for alkaline batteries, characterized in that it consists of
 - 5 (a) 0.0005-1% of aluminium,
 - (b) at least one of magnesium, strontium, barium and REM in such concentration that the ratio between Al, expressed in moles, and the sum of Mg, Sr, Ba and REM, expressed in moles, amounts at most to 2 and that the sum of the concentrations of Al, Mg, Sr, Ba and REM amounts at most to 2%,
 - 10 (c) 0.001-2% of at least one of bismuth, indium and gallium,
 - (d) possibly calcium in such concentration that the ratio between Al, expressed in moles, and the sum of Ca, Mg, Sr, Ba and REM, expressed in moles, amounts at most to 2, and that the sum of the concentrations of Al, Ca, Mg, Sr, Ba and REM amounts at most to 2%,
 - 15 (e) the remainder being zinc ;
excluded being the aluminium-containing zinc powder consisting of Zn, 0.003 % Al, 0.01 % Sr, 0.003 % Bi and 0.05 % In.
2. Powder according to Claim 1, characterized in that the ratio between the number of moles of Al and the number of moles of Mg, Sr, Ba and/or REM and possibly Ca amounts at most to 1.5.
3. Powder according to Claim 2, characterized in that the molar ratio amounts at most to 1.
- 25 4. Powder according to Claim 1, 2 or 3, characterized in that the sum of the concentrations of Al and Mg, Sr, Ba and/or REM and possibly Ca amounts at most to 1%.
5. Powder according to Claim 4, characterized in that the sum amounts at most to 0.2%.
- 30 6. Powder according to one of Claims 1-5, characterized in that it comprises 10-1000 ppm Al.
7. Powder according to Claim 6, characterized in that it comprises 10-500 ppm Al.
- 35 8. Powder according to one of Claims 1-7, characterized in that it comprises exclusively Al, Mg, possibly Ca and at least one of Bi, In and Ga as alloying elements.
9. Powder according to one of Claims 1-7, characterized in that it comprises exclusively Al, Sr, possibly Ca and at least one of Bi, In and Ga as alloying elements.

10. Powder according to one of Claims 1-7, characterized in that it comprises exclusively Al, Ba, possibly Ca and at least one of Bi, In and Ga as alloying elements.
- 5 11. Powder according to one of Claims 1-7, characterized in that it comprises exclusively Al, REM, possibly Ca and at least one of Bi, In and Ga as alloying elements.
12. Powder according to one of Claims 1-7 and 11, characterized in that REM is a mixed metal.
- 10 13. Powder according to one of Claims 1-12, characterized in that it comprises 20-1000 ppm Bi.
14. Powder according to Claim 13, characterized in that it comprises 20-500 ppm Bi.
- 15 15. Powder according to one of Claims 1-14, characterized in that it comprises 20-1000 ppm In.
16. Powder according to Claim 15, characterized in that it comprises 20-500 ppm In.
- 20 17. Powder according to one of Claims 1-16, characterized in that it comprises 10-1000 ppm Ga.
18. Powder according to Claim 17, characterized in that it comprises 10-500 ppm Ga.
- 25 19. Powder according to one of Claims 1-18, characterized in that it comprises up to 20 ppm of iron as impurity.
20. Powder according to Claim 19, characterized in that it comprises at most 10 ppm Fe.
- 30 21. Powder according to Claim 20, characterized in that it comprises at most 5 ppm Fe
22. Powder according to Claim 21, characterized in that it comprises at most 3 ppm Fe
- 35 23. Alkaline battery comprising an anode, a cathode and an electrolyte, characterized in that the anode comprises as active material a powder according to one of Claims 1-22.
24. Alkaline battery according to Claim 23, characterized in that the powder comprises metal cemented from the electrolyte.

25. Alkaline battery according to claim 23 or claim 24, characterized in that the battery is of the sealed type.

INTERNATIONAL SEARCH REPORT

Int. Application No
PCT/EP 95/03350

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C22C18/04 H01M4/42

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C22C H01M

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	EP,A,0 427 315 (S.A.ACEC-UNION MINIERE N.V.) 15 May 1991 cited in the application ---	1,4,6
Y	PATENT ABSTRACTS OF JAPAN vol. 18, no. 195 (E-1533) 5 April 1994 & JP,A,06 005 284 (TOSHIBA BATTERY CO.LTD.) 14 January 1994 see abstract ---	1,4,6
A	EP,A,0 172 255 (MITSUI MINING & SMELTING CO.LTD.) 26 February 1986 *Claims 1,2* --- -/--	1-24

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

15 November 1995

Date of mailing of the international search report

0 5. 12. 95

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INTERNATIONAL SEARCH REPORT

Int. Local Application No
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C/(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>PATENT ABSTRACTS OF JAPAN vol. 11, no. 220 (E-524) 16 July 1987 & JP,A,62 040 162 (MITSUI MINING & SMELTING CO.LTD.) 21 February 1987 see abstract</p> <p>-----</p>	1

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Information on patent family members

International Application No

PCT/EP 95/03350

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